



(11)

PATENT SPECIFICATION ⁽²¹⁾

50,192 /72

Class (52) 07. 0

Int. Cl. (51) C23C

Application Number (21) 50192/72
Lodged (22) 20th December, 1971

Complete Specification
entitled (54) COMPOSITION AND PROCESS.

Lodged (23) 15th December, 1972
Accepted (44) Lapsed Section 47c(b)
Published (41) 20th June, 1974

Convention Priority (30) Nil

Applicant (71) ICI AUSTRALIA LIMITED

Actual Inventor (72) ERWIN GUNTHER WALLICZEK

Related Art (56) Nil

The following statement is a full description of this invention, including the best method of performing it known to us :

This invention relates to the immersion plating of a metal coating on a second metal by chemical displacement from solution.

There are many applications in which an adherent coating of one metal on another is required. These coatings are often required to satisfy a temporary function; in such cases they may be quite thin but must be easy and cheap to apply. For example, ferrous wires or welding rods are sometimes coated with copper which acts as a temporary corrosion preventive. Similar copper coatings serve as a lubricant in the drawing of ferrous wire. In the carburising process, steel components are often copper plated in selected areas to prevent carburisation at specific locations. In electroplating, copper is commonly used as an underlayer for other plated metals. The electroplating of copper itself on a ferrous metal involves a precoating step in which the copper is electrolytically deposited onto the ferrous metal from solutions which commonly contain complex copper cyanides. The cyanide plating solutions are very toxic and effluents from the plating baths present a pollution problem; furthermore, these systems are seldom operated at high efficiencies and must be used hot for best results.

It is known that a first metal may be deposited onto a less noble second metal substrate when the metal substrate is brought into contact with an aqueous solution comprising the simple ions of the first metal. The quality of such a metal plating is however in most cases extremely poor. Thus, for example, when aqueous copper sulphate solution is contacted with iron a coating of copper is deposited onto the surface of the iron, but this coating has poor adherence and no practical

utility for the purposes illustrated above.

In the past, plating by chemical displacement of the metal in solution by the substrate metal, called immersion plating, has not achieved widespread use because of the non-adherent, dull or tarnishing properties of the deposited metal layer. We have now found a novel composition which can be used to produce high quality metal plating on certain metal substrates and in which the plating metal may be displaced from solution by the substrate metal during immersion in the plating bath, without requiring the use of electric current or added chemical reducing agents.

Accordingly we provide a solution for the immersion plating of a metal substrate with a plating metal, which solution comprises an anionic complex of the plating metal and a polyether containing from 2 - 200 inclusive ether groups.

The plating solutions of our invention may optionally comprise water.

The anionic complex may be formed by interaction of a simple metal ion with anion ligands such as halide, thiocyanate, sulphite, thiosulphate, phosphate or an organic anion. In addition the anionic complex may optionally contain a nonionic ligand such as carbon monoxide, sulphur dioxide, or nonionic organic compounds.

The anionic complex ions are associated in the plating solutions of our invention with equivalent concentrations of cations. The nature of the associated cations is not critical; suitable cations are, for example, the ions of hydrogen, of

50 192/72
alkali metals, of alkaline earth metals, or ammonium ions. In addition, during the plating process, other cations, for example, ferrous ions, are introduced into the solution as the result of dissolution of the substrate metal.

In order to achieve the best quality of plated metal and rate of plating it is in some cases desirable to include in the plating solution a source of hydrogen ions, such as sulphuric acid or sulphurous acid.

Optionally the polyether may be substituted with cyano, phosphate, sulphate, ester or carboxy groups. Preferably the polyether is a condensate of ethylene oxide, propylene oxide, or butylene oxide or mixtures thereof.

More preferred are polyoxyalkylene condensates comprising aliphatic alcohols containing from 1 to 24 carbon atoms, alkyl phenols, and fatty acids, condensed with polyoxyethylene or polyoxypropylene optionally cocommended either sequentially or randomly with higher alkylene oxides such as propylene oxide or butylene oxide.

Typical examples of preferred polyethers are:
methanol condensed with 2 moles of ethylene oxide; ethanol condensed with 2 or 3 moles of ethylene oxide; butanol condensed with 2 to 4 moles of ethylene oxide; methanol condensed sequentially or randomly with 2-6 moles of ethylene oxide and/or 2 to 6 moles of propylene oxide; C4-C10 saturated, branched or linear, alkyl alcohols condensed with 2-10 moles of ethylene oxide and optionally sequentially or randomly 2-10 moles of propylene oxide or butylene oxide; C10-C20, branched or linear, alcohols with 4-20 moles of ethylene oxide and optionally sequentially

50 192 /72

or randomly 2-20 moles of propylene oxide or butylene oxide; C4-20 alkyl phenols, C8-20 fatty acids, C8-20 fatty amides, C8-20 fatty amines, or di-phenylol propane, each condensed with 4-20 moles of ethylene oxide and optionally, either sequentially or by random addition, 4-20 moles of propylene oxide or butylene oxide; polypropylene glycol of molecular weight 900-4000 condensed with 10 to 90% of the total molecule by weight with ethylene oxide. All these materials may be optionally cyano ethylated with acrylonitrile.

In a preferred embodiment of our invention for use in the copper plating of ferrous substrates, the plating solution comprises a complex of copper in the cuprous state and a polyether as defined hereinbefore. An advantage of using a composition with copper in the cuprous state is that for the deposition of a given amount of copper only half the quantity of the substrate metal is dissolved compared with the case using copper in the cuprous state.

The proportion of copper in the plating composition is in the range from 0.01 to 12 percent by weight, preferably from 0.05 to 8 percent by weight. The proportion of the polyether is in the range from 5 to 99 percent by weight, preferably from 40 to 95 percent by weight.

For the best quality of copper plate on a ferrous substrate, it is necessary to maintain the copper in the cuprous state. While this may be achieved by exclusion of air from the system, it can be achieved conveniently by adding a reducing agent to the plating solution.

Preferably the plating solutions of our invention comprise sulphur dioxide. The reducing agent expressed as equivalent sulphur dioxide can be in the range from 0.05 to 15 percent by weight, preferably from 0.2 to 5 percent by weight.

The rate of plating may be increased by the optional inclusion of an acid such as sulphuric acid in the plating solution. The maximum concentration of acid which can be used will, however, be limited by the concentrations of sulphur dioxide and other components of the solution. The pH of the plating composition can be in the range from 0.3 to 4.5, preferably from 1.0 to 2.5.

Plating can be satisfactorily carried out at ambient temperatures with the compositions of this invention, but can also be carried out effectively at temperatures other than ambient if this is considered preferable from overall considerations of quality, throughput and cost.

For plating of copper onto ferrous metals we prefer that the anionic complex in the plating solutions of our invention is a chloride complex of cuprous copper. The copper coatings obtained are very bright and do not tarnish readily; they are strongly adherent to the substrate metal, and are consequently very suitable as a base coating, e.g. for subsequent application of further plating of the same or other metals.

The nature and concentrations of the copper complex, the polyether, and the other components of the solution, the temperature, and the properties of the substrate metal, are all interdependent in particular applications.

Suitable combinations may be found by simple experiment.

Although homogenous solutions have some practical convenience, the aims of the invention can be satisfactorily achieved with suitable compositions in the form of dispersions of one liquid phase in another.

The plating solutions of this invention can be applied to the surface of the substrate metal in various ways, for example, by immersion, by spraying, or by rubbing or brushing the solution on to the surface. The best method for any particular surface may be found by simple experiment.

During the plating operation there will be an accumulation of iron compounds in the plating solution. These can be readily removed from the spent solution by contacting it with a concentrated aqueous solution of either sodium chloride or sodium sulphate, whereupon the iron compounds will be transferred to the aqueous phase, and the purified polyether which is substantially insoluble, can be separated from the aqueous phase. Where the solubility of the polyether in the aqueous phase is lower at temperatures above ambient, advantage can be taken of this property by carrying out the washing and separation at an elevated temperature. The washed polyether can readily be recharged with the cuprous chloride complex and other components to prepare fresh plating solution. Since the polyether used in these plating compositions can extract the cuprous chloride complex from concentrated aqueous solutions of various inorganic chlorides, the washing and recharging with copper of the spent solution may also be carried out in a continuous manner.

50 192 /72

In a second preferred embodiment of our invention, plating solutions are provided for the plating of gold, silver and the platinum metals on to certain less noble metal substrates. We have found for example that the chloride complexes of gold, silver and the platinum metals, in the presence of polyethers containing two or more ether groups, are suitable for plating the respective metals onto copper or nickel surfaces. The copper surface to be plated with the more noble metal may itself have been plated onto a ferrous or other suitable metal substrate using the compositions of this invention.

50 192 /72

Certain of these solutions will give a bright adherent deposit of noble metal; the solution may be altered slightly to give a dull adherent deposit. The deposit of certain of these metals has been found to be a highly active catalyst. The production and use of these highly active catalysts constitutes a further aspect of our invention.

The main object of this invention is to enable the plating of metals on other metals by chemical displacement. The average thickness of the bright plated metal coatings so obtained is typically 0.2 to 0.7 micron. However, by the inclusion of a suitable reducing agent, such as formaldehyde, the compositions of this invention can be used to give thicker coatings by "electroless" deposition on metals or on non-metallic surfaces prepared in the conventional way known in the art for "electroless" plating.

The invention is now illustrated by, but by no means limited to, the following examples in which all parts are parts by weight unless otherwise specified.

Example 1

Cuprous chloride was dissolved to the limit of its solubility in a solution saturated with both sodium chloride and sulphur dioxide at room temperature. This solution was treated in the following general manner to extract the cuprous chloride complex substantially into an organic phase.

A sample (20 ml) of the saturated solution was mixed with the polyether (20 ml) at room temperature. On standing, the mixture separated into two phases. The organic phase was removed from the aqueous phase. Copper plating tests were carried out by dipping a clean plate of mild steel into the

50 192 /72

organic solution. In all cases the copper plating on the steel was bright and adherent. The polyethers used are shown in Table I.

TABLE I

Experiments	Polyether
1	'UCON 660' (Registered Trade Mark for a polyalkoxylated alcohol).
2	$\text{NC}-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}-\text{OCH}_2-\text{CH}_2-\text{CN}$
3	$\text{CH}_3-\text{O}-(\text{CH}_2-\text{CH}_2-\text{O})_2-\text{CH}_2-\text{CH}_2-\text{CN}$
4	A condensate of 4 moles ethylene oxide and 2 moles propylene oxide with 1 mole methanol.
5	A condensate of 4 moles ethylene oxide and 4 moles propylene oxide with 1 mole methanol.
6	A condensate of 11 moles ethylene oxide with 1 mole nonylphenol.
7	Polyethylene glycol of average molecular weight 1500.
8	$\left[\text{CH}_3\text{O}(\text{CH}_2-\text{CH}_2-\text{O})_3 \right]_3 \text{B}$
9	$\text{CH}_3\text{O}(\text{CH}_2-\text{CH}_2-\text{O})_2-\text{CH}_2-\text{CH}_2-\text{CO}_2(\text{CH}_2-\text{CH}_2\text{O})_2\text{CH}_3$

Example 2

A solution of a complex cuprous chloride was made by dissolving 12 g. sodium chloride and 10 g. cuprous chloride in 30 g. water and 220 g. of a condensate of 4 moles ethylene oxide and 2 moles propylene oxide with 1 mole methanol. An additional 50 g. water was added and sulphur dioxide was added

50 192 /72

to make its concentration 0.4% by weight.

Clean strips of mild steel were immersed in this solution for 5 minutes at ambient temperature (about 22°C.), removed and washed with water. The resultant copper plate was 0.25 micron thick and was bright and very adherent, showing no tendency to removal from the steel surface when tested by contacting it with a strip of strongly adhesive tape and then pulling off the tape at right angles to the surface.

Example 3

This example compares the quality of copper plating achieved with the compositions of our invention with comparative immersion plating solutions not of our invention using copper in the cupric state.

The plating solutions had the following compositions:

Solution A of our invention - 12 parts sodium chloride, 10 parts cuprous chloride, 80 parts water, 220 parts condensate of 4 moles ethylene oxide and 2 moles propylene oxide with 1 mole methanol, 3.9 parts sulphuric acid, 1.6 parts sulphur dioxide.

Solution B not of our invention - 12 parts sodium chloride, 13.6 parts cupric chloride, 80 parts water, 220 parts condensate of 4 moles ethylene oxide and 2 moles propylene oxide with 1 mole methanol.

Solution C not of our invention - 24 g/l $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 30 g/l NaCl, 30 ml/l H_2SO_4 (98%), 4 g/l ethylene oxide condensate of a fatty amine having 16 carbon atoms with 5 ethylene oxide units.

Solution D not of our invention - 40 g/l $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$,

50 192/72

220 g/l H_2SO_4 , 70 g/l HCl , 17 g/l NH_4Cl , 25 g/l polyoxyethylene lauryl ether.

Mild steel strips were prepared by immersion for five minutes at room temperature in a solution containing 20 parts concentrated hydrochloric acid, 80 parts water and 0.2 parts of a pickling inhibitor ("Galvene", Trade Mark for a pickling inhibitor), followed by thorough washing with water.

Plating tests were carried out by immersion of the steel strips in the solutions for one minute at ambient temperature (about 22°C). The adherence of the plated metal to the substrate metal was tested by the adhesive tape method described in Example 2. The results are shown in Table II.

TABLE II

Solution No.	Properties of Plated Copper	
	Appearance	Adherence
A	Bright	Completely adherent
B	Dull, black	Substantially stripped off
C	Dull	Partly removed
D	Fairly bright	Partly removed

Example 4

Copper plating solutions were made by dissolving sodium chloride and cuprous chloride in the weight ratio 1.2 : 1, to give the required copper content in solutions containing water and a condensate of 4 moles of ethylene oxide and 2 moles of propylene oxide with 1 mole of methanol. Sulphur dioxide was added to each solution. Copper plating tests were carried out, unless otherwise noted, by immersion of clean mild steel

50 192 /72
strips in the solutions for five minutes.

The average thickness of copper deposited was measured by chemical solution and analysis. The compositions of the solutions, the plating temperature, and observations on the properties of the plating are recorded in Table III. Adherence was good in all cases as evaluated by the adhesive tape test.

50.192/72
TABLE III

Solution Composition							
% w/v copper	% w/v alkoxylate	% w/v water	% w/v Sulphur Dioxide	Plating Temperature °C	Plate Thickness (Micron)	Plate Quality	Notes
2.9	77	8	1.2	20	0.23	Bright, adherent	
2.4	63	25	1.0	20	0.61	Bright, adherent	1
2.4	63	25	1.0	20	1.3	Bright, adherent	2
2.0	69	24	0.3	20	0.25	Bright, adherent	
2.0	69	24	0.3	45	0.30	Bright, adherent	

- Notes:
1. Solution was applied to the steel surface by rubbing on.
 2. Solution also contained 0.6% formaldehyde, and time of immersion was 15 minutes.

Example 5

A solution of 0.2 g chloroplatinic acid in 10 ml of a condensate of 4 moles ethylene oxide and 2 moles propylene oxide with 1 mole methanol was applied by immersion of a copper surface for 14 minutes at ambient temperature (about 20°C). The copper surface had itself been prepared by plating copper onto a ferrous substrate in the manner of Example 2.

The resultant platinum plating was bright and adherent. The deposited platinum had high catalytic hydrogenation activity.

Example 6

A solution was prepared containing the following components: 12 g sodium chloride, 10 g cuprous chloride, 80 ml water and 220 ml of a condensate of 4 moles ethylene oxide and 2 moles propylene oxide with 1 mole methanol. To portions of this solution various acidic components were added in the proportions shown in Table IV. Clean strips of mild steel were immersed in each of the resulting solutions for three minutes at the selected temperature. The appearance of the copper plate and its adhesion to the steel surface, as measured by the adhesive tape test, are shown in Table IV.

50.192/72

TABLE IV

Acid g/l	Sulphur dioxide g/l	pH	Temp °C	Quality of Copper Plate	
				Appearance	Adherence
nil	nil	4.6	20	Dark	Poor
nil	5	2.0	20	Bright	Adherent
nil	5		45	Bright	Adherent
nil	10		20	Bright	Adherent
H ₂ SO ₄ , 1.5	nil		20	Slight discolor- ation	Adherent
H ₂ SO ₄ , 1.5	nil		45	Bright	Adherent
H ₂ SO ₄ , 1	5	1.6	20	Bright	Adherent
H ₂ SO ₄ , 10	5	1.0	20	Discolor- ation	Adherent
H ₂ SO ₄ , 30	5	0.4	20	Dark	Poor
HCl, 1	5		45	Dark	Poor
HCl, 5	nil		20	Discolor- ation	Partly removed

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:-

1. A solution for the immersion plating of a metal substrate with a plating metal, which solution comprises an anionic complex of the plating metal and a polyether containing from 2 to 200 inclusive ether groups.
2. A solution according to Claim 1 wherein the polyether is a condensate of ethylene oxide, propylene oxide, butylene oxide or mixtures thereof.
3. A solution according to Claims 1 or 2 wherein the polyether is a condensate of an alkylene oxide with an aliphatic alcohol containing from 1 to 24 carbon atoms, an alkyl phenol or a fatty acid.
4. A solution according to any one of Claims 1 to 3 wherein the polyether is chosen from the group consisting of a condensate of an aliphatic alcohol containing 1 to 10 carbon atoms with 2 to 10 moles of alkylene oxide containing 2 to 3 carbon atoms and cyanoethylated derivatives thereof.
5. A solution according to any one of Claims 1 to 4 inclusive for plating ferrous substrates wherein the solution comprises a complex of cuprous copper.
6. A solution according to Claim 5 wherein the proportion of copper in the solution is in the range from 0.01 to 12% by weight.

7. A solution according to Claim 6 wherein the proportion of copper in the solution is in the range from 0.05 to 8% by weight.
8. A solution according to any one of Claims 5 to 7 inclusive wherein the proportion of polyether in the solution is in the range from 5 to 99% by weight.
9. A solution according to Claim 8 wherein the proportion of polyether in the solution is in the range from 40 to 95% by weight.
10. A solution according to any one of Claims 5 to 9 inclusive wherein the solution comprises a reducing agent expressed as equivalent sulphur dioxide in the range from 0.05 to 15% by weight.
11. A solution according to Claim 10 wherein the solution comprises a reducing agent expressed as equivalent sulphur dioxide in the range from 6.2 to 5% by weight.
12. A solution according to any one of Claims 5 to 11 inclusive wherein the pH is in the range 0.3 to 4.5.
13. A solution according to Claim 12 wherein the pH is in the range from 1.0 to 2.5.

50 192 /72

14. A solution according to any one of Claims 5 to 13 inclusive wherein the copper complex is a chloride complex.
15. A solution according to any one of Claims 1 to 4 which solution comprises chloride complexes of gold, silver or platinum.
16. A process of plating metals comprising treating a suitable substrate metal with a solution according to any one of Claims 1 to 15 inclusive.
17. A solution according to Claim 1 substantially as described with reference to the examples.
18. A process of plating metal according to Claim 16 substantially as described with reference to the examples.

DATED this 13/4 day of October, 1972

ICI AUSTRALIA LIMITED



50,192 /72